

苦皮藤根皮的化学成分

朱文丽^{1,2}, 沈国鹏¹, 张海艳², 赵天增^{2*}

(1. 郑州大学 化工与能源学院, 郑州 450001; 2. 河南省科学院天然产物重点实验室, 郑州 450002)

[摘要] 目的: 研究苦皮藤根皮醇提物的化学成分。方法: 采用硅胶柱色谱和高效液相分离纯化, 通过 NMR 鉴定化合物的结构。结果: 分离并鉴定了 11 个化合物, 分别为 celahin B(1), celastrine A(2), celahin D(3), 苦皮素 E(4), 苦皮素 A(5), celangulatin C(6), 苦皮藤素 XIX(7), 苦皮素 P(8), 苦皮素 H(9), 苦皮藤素 III(10), 苦皮素 J(11)。结论: 化合物 1~3 为首次从苦皮藤中分离得到。

[关键词] 苦皮藤; 醇提物; 化学成分; 分离鉴定

[中图分类号] R284.1 **[文献标识码]** A **[文章编号]** 1005-9903(2011)14-0117-06

Chemical Constituents of Root Barks of *Celastrus angulatus*

ZHU Wen-li^{1,2}, SHEN Guo-peng¹, ZHANG Hai-yan², ZHAO Tian-zeng^{2*}

(1. Department of Chemical and Energy Engineering, Zhengzhou University, Zhengzhou 450001, China;
2. Key Laboratory of Natural Products, Henan Academy of Science, Zhengzhou 450002, China)

[Abstract] **Objective:** To study the chemical constituents from the alcohol extract of root bark of *Celastrus angulatus*. **Method:** The compounds, whose structures were confirmed by NMR spectra, were separated and purified by silica gel and preparative HPLC. **Result:** The structures of eleven compounds were conformed, they were celahin B(1), celastrine A(2), celahin D(3), angulatin E(4), angulatin A(5), celangulatin C(6), celangulin XIX(7), angulatin P(8), angulatin H(9), celangulin III(10), and angulatin J(11). **Conclusion:** Compound 1-3 were first found in *C. angulatus*.

[Key words] *Celastrus angulatus*; alcohol extract; chemical constituents; isolation and identification

[收稿日期] 20110211(007)

[基金项目] 河南省发改委产业化研发专项(2060403)

[第一作者] 朱文丽, 硕士研究生, 研究方向: 天然产物化学

[通讯作者] * 赵天增, 研究员, 博士生导师, 研究方向: 天然产物化学和波谱解析, Tel: 0371-65353128, E-mail: tianzeng_zhao@163.com

性组分的优良方法。得到的主要成分 β -蛇床烯和 α -蛇床烯为首次从贵州金丝桃挥发油中发现; 石竹烯在文献中为痕量成分; 而文献报道的含量较高的 γ -衣兰油烯和石竹烯氧化物在本研究中的含量较低。

[参考文献]

[1] 中国科学院《中国植物志》编辑委员会. 中国植物志. 第 50 卷. 第 2 分册 [M]. 北京: 科学出版社, 1990: 31.

[2] 刘兴宽, 郁建平, 谷练权. 贵州金丝桃中黄酮类成分研究[J]. 中药材, 2005, 28(10): 893.

[3] 郁建平, 刘兴宽, 谷练权, 等. 贵州金丝桃挥发油成分及抗菌活性研究[J]. 中国药学杂志, 2002, 37(12): 900.

[4] 吴彩霞, 邢煜君, 曹乃峰, 等. 宜昌胡颓子挥发性成分的 HS-SPME-GC-MS 研究[J]. 中国实验方剂学杂志, 2010, 16(10): 53.

[5] 孙慧玲, 张倩, 李东, 等. 固相微萃取/气象色谱法分析锦鸡儿茎挥发性成分[J]. 中国实验方剂学杂志, 2010, 16(10): 63. **[责任编辑]** 邹晓翠

苦皮藤 *Celastrus angulatus* Maxim 亦叫马断肠、苦树皮、老虎麻等,系卫矛科 (Celastraceae) 南蛇藤属 *Celastrus* 多年生藤状灌木植物,产于河北、山东、河南、陕西、湖北、甘肃、江苏、安徽等省;其果皮和种子含油脂可供工业用,根皮及茎皮为杀虫剂和灭菌剂^[1]。研究证明其中所含的杀虫活性成分主要是以 β -二氢沉香呔喃骨架的多元醇酯化合物及其生物碱^[2-3]。

本文系统研究了苦皮藤根皮醇提物的化学成分。从苦皮藤根皮醇提物中分离得到了 11 个化合物,分别鉴定为 celahin B (1), celastrine A (2), celahin D (3), 苦皮素 E (angulatin E, 4), 苦皮素 A (angulatin A, 5), celangulatin C (6), 苦皮藤素 XIX (celangulin XIX, 7), 苦皮素 P (angulatin P, 8), 苦皮素 H (angulatin H, 9), 苦皮藤素 III (celangulin III, 10), 苦皮素 J (angulatin J, 11)。其中,化合物 1 ~ 3 为首次从该植物中分离得到。

1 材料

DPX 400 型核磁共振仪 (瑞士 Bruker 公司), Waters 600 半制备高效液相色谱仪 (美国沃特斯科技术有限公司), 柱色谱及薄层色谱用硅胶 (青岛海洋化工厂)。

苦皮藤根皮 2009 年 6 月购自陕西省药材市场,经河南省农业大学朱长山教授鉴定为 *C. angulatus*。

2 提取与分离

称取 1 kg 苦皮藤根皮粉末,依次加入 3:2:2 倍量 95% 乙醇 80 °C 下回流提取 2 h,过滤,合并 3 次滤液,减压浓缩至浸膏。按此方法共提取苦皮藤根皮粉末 7 kg,总共得浸膏 2 570 g。称取上述醇提物浸膏 1 120 g,加入 6 倍量三氯甲烷,80 °C 下回流提取 40 min,过滤,减压浓缩至浸膏,得浸膏 147 g。此浸膏硅胶拌样后上柱,采用石油醚-乙酸乙酯 (10:1 ~ 4:6) 进行梯度洗脱,经高效液相制备纯化 [Sunfire C₁₈ 色谱柱 (10 mm × 150 mm, 10 μm); 流动相甲醇-水,柱温 25 °C,流速 10 mL · min⁻¹,检测波长 232 nm,进样量 200 μL] 共得到 11 个化合物。第 228 ~ 239 份经制备纯化 (甲醇-水,70:30) 得化合物 1 (15 mg); 第 261 ~ 271 份经制备纯化 (甲醇-水,68:32) 得化合物 2 (14 mg); 第 280 ~ 281 份经制备纯化 (甲醇-水,65:35) 得化合物 3 (25 mg); 第 381 ~ 385 份经制备纯化 (甲醇-水,65:35) 得化合物 4 (27 mg); 第 420 份经制备纯化 (甲醇-水,62:38) 得化合物 5 (80

mg); 第 546 ~ 554 份经制备纯化 (甲醇-水,60:40) 得化合物 6 (57 mg) 和化合物 7 (43 mg); 第 590 ~ 594 份经制备纯化 (甲醇-水,68:32) 得化合物 8 (16 mg); 第 613 ~ 614 份经制备纯化 (甲醇-水,62:38) 得化合物 9 (60 mg); 第 679 ~ 681 份经制备纯化 (甲醇-水,60:40) 得化合物 10 (26 mg); 第 820 份经制备纯化 (甲醇-水,68:32) 得化合物 11 (29 mg)。

3 结构鉴定

化合物 1 白色无定形粉末。¹H-NMR (400 MHz, CDCl₃) δ_H: 5.71 (1H, d, J = 3.4 Hz, H-1), 5.58 (1H, m, H-2), 1.80 (1H, dd, J = 2.4, 14.8 Hz, H-3a), 2.44 (1H, m, H-3b), 2.38 (1H, m, H-4), 5.97 (1H, brs, H-6), 2.25 (1H, m, H-7), 2.22 (1H, m, H-8a), 2.52 (1H, m, H-8b), 5.41 (1H, J = 7.2 Hz, H-9), 1.42 (3H, s, H-12), 1.45 (3H, s, H-13), 1.19 (3H, d, J = 7.6 Hz, H-14), 4.36 (1H, d, J = 12.8 Hz, H-15a), 5.05 (1H, d, J = 12.8 Hz, H-15b), 1.55 [3H, s, OAC-1 (CH₃)], 2.08* [3H, s, OAC-2 (CH₃)], 2.11 [3H, s, OAC-6 (CH₃)], 2.25* [3H, s, OAC-15 (CH₃)], 8.04 [2H, m, OBz-9 (2', 6')], 7.44 [2H, m, OBz-9 (3', 5')], 7.57 [1H, m, OBz-9 (4')]. ¹³C-NMR (100 MHz, CDCl₃) δ_C: 71.5 (C-1), 69.5 (C-2), 30.8 (C-3), 33.1 (C-4), 89.2 (C-5), 78.1 (C-6), 48.8 (C-7), 34.8 (C-8), 69.4 (C-9), 53.3 (C-10), 82.7 (C-11), 30.3 (C-12), 25.9 (C-13), 17.8 (C-14), 65.4 (C-15); OAC-1: 169.3 (C = O), 20.4 (CH₃); OAC-2*: 170.0 (C = O), 21.3 (CH₃); OAC-6: 170.0 (C = O), 21.3 (CH₃); OAC-15*: 170.6 (C = O), 21.4 (CH₃); OBz: 165.3 (C = O), 129.1 (C-1'), 130.1 (C-2', 6'), 128.3 (C-3', 5'), 133.5 (C-4') (* 归属可互换)。以上 NMR 数据与文献[4]报道的 celahin B 数据一致。

化合物 2 白色透明状物质。¹H-NMR (400 MHz, CDCl₃) δ_H: 5.41 (1H, brd, J = 4.8, 11.8 Hz, H-1), 1.67 (1H, m, H-2a), 1.76 (1H, m, H-2b), 1.50 (1H, m, H-3a), 2.19 (1H, m, H-3b), 2.25 (1H, m, H-4), 6.67 (1H, brs, H-6), 2.43 (1H, brd, J = 4.1 Hz, H-7), 5.59 (1H, dd, J = 4.1, 5.8 Hz, H-8), 5.66 (1H, J = 5.8 Hz, H-9), 1.42 (3H, s, H-12), 1.58 (3H, s, H-13), 1.02 (3H, d, J = 7.5 Hz, H-14), 4.50 (1H, d, J = 13.2 Hz, H-15a), 5.02 (1H, d, J = 13.2 Hz, H-15b), 1.47 [3H, s, OAC-1 (CH₃)], 2.12 [3H,

s, OAC-6(CH₃)] , 2.04 [3H, s, OAC-8(CH₃)] , 2.30 [3H, s, OAC-15(CH₃)] , 8.04 [2H, m, OBz-9(2', 6')] , 7.46 [2H, m, OBz-9(3', 5')] , 7.57 [1H, m, OBz-9(4')]。¹³C-NMR(100 MHz, CDCl₃) δ_C: 79.4(C-1), 23.0(C-2), 26.3(C-3), 33.2(C-4), 90.6(C-5), 74.7(C-6), 52.9(C-7), 70.2(C-8), 72.7(C-9), 50.7(C-10), 81.1(C-11), 30.4(C-12), 24.5(C-13), 15.1(C-14), 60.3(C-15); OAC-1: 170.0(C=O), 20.7(CH₃); OAC-6: 169.8(C=O), 21.3(CH₃); OAC-8: 170.0(C=O), 21.0(CH₃); OAC-15: 170.6(C=O), 21.5(CH₃); OBz: 164.8(C=O), 129.4(C-1'), 129.6(C-2', 6'), 128.7(C-3', 5'), 133.4(C-4')。以上 NMR 数据与文献[5]报道的 celastrine A 数据一致。

化合物 3 白色无定形粉末。¹H-NMR(400 MHz, CDCl₃) δ_H: 5.72(1H, d, J = 3.8 Hz, H-1), 5.62(1H, m, H-2), 1.77(1H, m, H-3a), 2.55(1H, m, H-3b), 2.42(1H, m, H-4), 6.56(1H, brs, H-6), 2.55(1H, brd, J = 2.8 Hz, H-7), 5.54(1H, d, J = 2.8 Hz, H-8), 5.77(1H, s, H-9), 1.49(3H, s, H-12), 1.67(3H, s, H-13), 1.17(3H, d, J = 7.6 Hz, H-14), 4.62(1H, d, J = 12.9 Hz, H-15a), 5.15(1H, d, J = 12.9 Hz, H-15b), 1.48 [3H, s, OAC-1(CH₃)] , 2.08 [3H, s, OAC-2(CH₃)] , 2.13 [3H, s, OAC-6(CH₃)] , 2.05 [3H, s, OAC-15(CH₃)] , 8.18 [2H, m, OBz-8(2', 6')] , 7.48 [2H, m, OBz-8(3', 5')] , 7.59 [1H, m, OBz-8(4')] , 8.05 [2H, m, OBz-9(2', 6')] , 7.45 [2H, m, OBz-9(3', 5')] , 7.59 [1H, m, OBz-9(4')]。¹³C-NMR(100 MHz, CDCl₃) δ_C: 71.7(C-1), 69.2(C-2), 31.1(C-3), 32.8(C-4), 89.8(C-5), 75.0(C-6), 53.5(C-7), 77.7(C-8), 73.6(C-9), 52.7(C-10), 81.5(C-11), 30.4(C-12), 26.0(C-13), 16.7(C-14), 65.9(C-15); OAC-1: 169.3(C=O), 20.4(CH₃); OAC-2: 170.0(C=O), 21.3(CH₃); OAC-6: 169.7(C=O), 21.3(CH₃); OAC-15: 170.7(C=O), 21.2(CH₃); OBz-8: 165.5(C=O), 128.7(C-1'), 130.0(C-2', 6'), 128.4(C-3', 5'), 133.4(C-4'); OBz-9: 164.4(C=O), 129.9(C-1'), 130.2(C-2', 6'), 128.4(C-3', 5'), 133.7(C-4')。以上 NMR 数据与文献[6]报道的 celahin D 数据一致。

化合物 4 白色无定形粉末。¹H-NMR(400

MHz, CDCl₃) δ_H: 5.45(1H, d, J = 3.2 Hz, H-1), 5.35(1H, m, H-2), 1.97(1H, dd, J = 2.3, 14.9 Hz, H-3a), 2.07(1H, dd, J = 3.3, 14.9 Hz, H-3b), 5.17(1H, s, H-6), 2.56(1H, d, J = 3.0 Hz, H-7), 5.55(1H, dd, J = 3.0, 9.8 Hz, H-8), 6.03(1H, d, J = 9.8 Hz, H-9), 1.57(3H, s, H-12), 1.68(3H, s, H-13), 1.72(3H, s, H-14), 4.55(1H, d, J = 13.4 Hz, H-15a), 4.90(1H, d, J = 13.4 Hz, H-15b), 1.51 [3H, s, OAC-1(CH₃)] , 2.07 [3H, s, OAC-2(CH₃)] , 2.33 [1H, sept, J = 7.0 Hz, OiBu-8(CH)] , 0.88 [3H, d, J = 7.0 Hz, OiBu-8(CH₃)] , 0.91 [3H, d, J = 7.0 Hz, OiBu-8(CH₃)] , 2.62 [1H, sext, J = 7.0 Hz, O(α-Me)Bu-15(CH)] , 1.59, 1.82 [各 1H, m, O(α-Me)Bu-15(CH₂)] , 0.98 [3H, t, J = 7.0 Hz, O(α-Me)Bu-15(CH₃)] , 1.29 [3H, d, J = 7.0 Hz, O(α-Me)Bu-15(CH₃)] , 7.83 [2H, m, OBz-9(2', 6')] , 7.36 [2H, m, OBz-9(3', 5')] , 7.51 [1H, m, OBz-9(4')] , 3.07(1H, brs, OH-4), 5.17(1H, brs, OH-6)。¹³C-NMR(100 MHz, CDCl₃) δ_C: 75.1(C-1), 67.3(C-2), 41.2(C-3), 72.2(C-4), 91.5(C-5), 76.9(C-6), 53.5(C-7), 73.8(C-8), 75.2(C-9), 50.5(C-10), 84.5(C-11), 30.1(C-12), 26.3(C-13), 24.1(C-14), 61.7(C-15); OAC-1: 169.6(C=O), 20.5(CH₃); OAC-2: 169.5(C=O), 21.1(CH₃); OiBu: 175.7(C=O), 34.1(CH), 18.5(CH₃), 18.6(CH₃); O(α-Me)Bu: 176.2(C=O), 41.6(CH), 26.6(CH₂), 11.7(CH₃), 16.9(CH₃); OBz: 165.7(C=O), 129.4(C-1'), 129.5(C-2', 6'), 128.6(C-3', 5'), 133.4(C-4')。以上 NMR 数据与文献[7]报道的 1β, 2β-diacetoxy-4α, 6α-dihydroxy-8α-isobutanoyloxy-9β-benzoyloxy-15-(α-methyl)-butanoyloxy-β-dihydroagrofuran 数据一致, 笔者称为苦皮素 E(angulatin E)。

化合物 5 白色针状结晶。¹H-NMR(400 MHz, CDCl₃) δ_H: 5.49(1H, d, J = 3.2 Hz, H-1), 5.39(1H, m, H-2), 2.01(1H, dd, J = 2.5, 14.9 Hz, H-3a), 2.09(1H, m, H-3b), 5.21(1H, brd, J = 5.1 Hz, H-6), 2.58(1H, brd, J = 2.9 Hz, H-7), 5.62(1H, dd, J = 2.9, 9.8 Hz, H-8), 6.06(1H, d, J = 9.8 Hz, H-9), 1.61(3H, s, H-12), 1.72(3H, s, H-13), 1.78(3H, s, H-14), 4.65(1H, d, J = 13.4 Hz, H-15a), 4.87(1H, d, J = 13.4 Hz, H-15b), 1.55 [3H, s, OAC-1(CH₃)] , 2.11 [3H, s, OAC-2(CH₃)] , 2.38 [1H,

sept, $J = 7.0$ Hz, OiBu-8 (CH)], 0.92 [3H, d, $J = 7.0$ Hz, OiBu-8 (CH₃)], 0.95 [3H, d, $J = 7.0$ Hz, OiBu-8 (CH₃)], 2.85 [1H, sept, $J = 7.0$ Hz, OiBu-15 (CH)], 1.348 [3H, d, $J = 7.0$ Hz, OiBu-15 (CH₃)], 1.351 [3H, d, $J = 7.0$ Hz, OiBu-15 (CH₃)], 7.85 [2H, m, OBz-9 (2', 6')], 7.41 [2H, m, OBz-9 (3', 5')], 7.55 [1H, m, OBz-9 (4')], 3.12 (1H, brs, OH-4), 5.23 (1H, brd, $J = 5.1$ Hz, OH-6)。¹³C-NMR (100 MHz, CDCl₃) δ_c : 75.0 (C-1), 67.3 (C-2), 41.2 (C-3), 72.1 (C-4), 91.4 (C-5), 76.9 (C-6), 53.5 (C-7), 73.7 (C-8), 75.3 (C-9), 50.5 (C-10), 84.5 (C-11), 30.0 (C-12), 26.4 (C-13), 24.1 (C-14), 61.7 (C-15); OAC-1: 169.5 (C=O), 20.5 (CH₃); OAC-2: 169.6 (C=O), 21.1 (CH₃); OiBu-8: 175.8 (C=O), 34.1 (CH), 18.5 (CH₃), 18.7 (CH₃); OiBu-15: 176.8 (C=O), 34.3 (CH), 19.1 (CH₃), 19.1 (CH₃); OBz: 165.7 (C=O), 129.3 (C-1'), 129.4 (C-2', 6'), 128.6 (C-3', 5'), 133.4 (C-4')。以上 NMR 数据与文献 [8] 报道的苦皮素 A (angulatin A) 数据一致。

化合物 6 白色无定形粉末。¹H-NMR (400 MHz, CDCl₃) δ_H : 5.47 (1H, d, $J = 3.4$ Hz, H-1), 5.39 (1H, m, H-2), 2.00 (1H, dd, $J = 2.7, 14.9$ Hz, H-3a), 2.11 (1H, m, H-3b), 5.20 (1H, brd, $J = 5.0$ Hz, H-6), 2.61 (1H, brd, $J = 3.2$ Hz, H-7), 5.60 (1H, dd, $J = 3.2, 9.8$ Hz, H-8), 6.04 (1H, d, $J = 9.8$ Hz, H-9), 1.61 (3H, s, H-12), 1.72 (3H, s, H-13), 1.78 (3H, brs, H-14), 4.66 (1H, d, $J = 13.4$ Hz, H-15a), 4.86 (1H, d, $J = 13.4$ Hz, H-15b), 1.53 [3H, s, OAC-1 (CH₃)], 2.11 [3H, s, OAC-2 (CH₃)], 1.89 [3H, s, OAC-8 (CH₃)], 2.84 [1H, sept, $J = 6.9$ Hz, OiBu-15 (CH)], 1.34 [3H, d, $J = 6.9$ Hz, OiBu-15 (CH₃)], 1.35 [3H, d, $J = 6.9$ Hz, OiBu-15 (CH₃)], 7.87 [2H, m, OBz-9 (2', 6')], 7.42 [2H, m, OBz-9 (3', 5')], 7.57 [1H, m, OBz-9 (4')], 3.15 (1H, brs, OH-4), 5.24 (1H, brs, OH-6)。¹³C-NMR (100 MHz, CDCl₃) δ_c : 75.1 (C-1), 67.3 (C-2), 41.2 (C-3), 72.1 (C-4), 91.4 (C-5), 76.9 (C-6), 53.5 (C-7), 74.2 (C-8), 75.3 (C-9), 50.6 (C-10), 84.6 (C-11), 30.0 (C-12), 26.3 (C-13), 24.2 (C-14), 61.7 (C-15); OAC-1: 169.5 (C=O), 20.4 (CH₃); OAC-2: 169.4 (C=O), 21.1 (CH₃); OAC-8: 170.0 (C=O), 20.8 (CH₃); OiBu: 176.7 (C=O), 34.3 (CH), 19.0 (CH₃), 19.1

(CH₃); OBz: 165.6 (C=O), 129.3 (C-1'), 129.5 (C-2', 6'), 128.7 (C-3', 5'), 133.5 (C-4')。以上 NMR 数据与文献 [9] 报道的 celangulatin C 数据一致。

化合物 7 白色无定形粉末。¹H-NMR (400 MHz, CDCl₃) δ_H : 5.53 (1H, d, $J = 3.4$ Hz, H-1), 5.39 (1H, m, H-2), 2.03 (1H, dd, $J = 2.8, 15.0$ Hz, H-3a), 2.13 (1H, dd, $J = 3.4, 15.0$ Hz, H-3b), 5.26 (1H, brd, $J = 3.1$ Hz, H-6), 2.78 (1H, brd, $J = 3.3$ Hz, H-7), 5.65 (1H, dd, $J = 3.3, 9.8$ Hz, H-8), 6.17 (1H, d, $J = 9.8$ Hz, H-9), 1.61 (3H, s, H-12), 1.76 (3H, s, H-13), 1.80 (3H, brs, H-14), 4.71 (1H, d, $J = 13.4$ Hz, H-15a), 4.89 (1H, d, $J = 13.4$ Hz, H-15b), 1.52 [3H, s, OAC-1 (CH₃)], 2.12 [3H, s, OAC-2 (CH₃)], 2.84 [1H, sept, $J = 7.0$ Hz, OiBu-15 (CH)], 1.34 [3H, d, $J = 7.0$ Hz, OiBu-15 (CH₃)], 1.35 [3H, d, $J = 7.0$ Hz, OiBu-15 (CH₃)], 7.82 [2H, m, OBz-9 (2', 6')], 7.38 [2H, m, OBz-9 (3', 5')], 7.52 [1H, m, OBz-9 (4')], 7.89 [1H, dd, $J = 0.6, 1.0$ Hz, OFu-8 (2')], 6.61 [1H, dd, $J = 0.6, 1.8$ Hz, OFu-8 (4')], 7.34 [1H, dd, $J = 1.0, 1.8$ Hz, OFu-8 (5')], 3.13 (1H, brs, OH-4), 5.23 (1H, d, $J = 3.1$ Hz, OH-6)。¹³C-NMR (100 MHz, CDCl₃) δ_c : 75.1 (C-1), 67.4 (C-2), 41.3 (C-3), 72.2 (C-4), 91.5 (C-5), 76.8 (C-6), 53.4 (C-7), 74.7 (C-8), 75.1 (C-9), 50.6 (C-10), 84.6 (C-11), 30.0 (C-12), 26.3 (C-13), 24.2 (C-14), 61.8 (C-15); OAC-1: 169.5* (C=O), 20.4 (CH₃); OAC-2: 169.6* (C=O), 21.2 (CH₃); OiBu: 176.7 (C=O), 34.4 (CH), 19.2 (CH₃), 19.2 (CH₃); OBz: 165.7 (C=O), 129.3 (C-1'), 129.5 (C-2', 6'), 128.6 (C-3', 5'), 133.4 (C-4'); OFu: 161.9 (C=O), 148.2 (C-2'), 118.6 (C-3'), 109.6 (C-4'), 143.9 (C-5')。(* 归属可互换)。以上 NMR 数据与文献 [7] 报道的 1 β , 2 β -diacetoxy-4 α , 6 α -dihydroxy-8 α -furoyloxy-9 β -benzoyloxy-15-iso-butanoyloxy- β -dihydroaga-rofuran (苦皮藤素 XIX) 数据一致。

化合物 8 白色无定形粉末。¹H-NMR (400 MHz, CDCl₃) δ_H : 5.62 (1H, d, $J = 3.6$ Hz, H-1), 5.56 (1H, m, H-2), 1.99 (1H, dd, $J = 2.6, 15.2$ Hz, H-3a), 2.24 (1H, dd, $J = 3.5, 15.2$ Hz, H-3b), 6.23 (1H, brs, H-6), 2.40 (1H, brd, $J = 2.9$ Hz, H-7), 5.29 (1H, d, $J = 2.9$ Hz, H-8), 5.70 (1H, s, H-9),

1.58(3H, s, H-12), 1.65(3H, s, H-13), 1.50(3H, s, H-14), 4.83(1H, d, $J = 12.7$ Hz, H-15a), 4.88(1H, d, $J = 12.7$ Hz, H-15b), 1.47 [3H, s, OAc-1(CH₃)], 2.07 [3H, s, OAc-2(CH₃)], 2.11 [3H, s, OAc-6(CH₃)], 2.68 [1H, sext, $J = 6.9$ Hz, OiBu-8(CH)], 1.26 [3H, d, $J = 6.9$ Hz, OiBu-8(CH₃)], 1.27 [3H, d, $J = 6.9$ Hz, OiBu-8(CH₃)], 2.58 [1H, sext, $J = 6.9$ Hz, O(α -Me)Bu-15(CH)], 1.58, 1.80 [各1H, m, O(α -Me)Bu-15(CH₂)], 0.97 [3H, t, $J = 7.4$ Hz, O(α -Me)Bu-15(CH₃)], 1.24 [3H, $J = 7.0$ Hz, O(α -Me)Bu-15(CH₃)], 8.00 [2H, m, OBz-9(2',6')], 7.45 [2H, m, OBz-9(3',5')], 7.60(1H, m, OBz-9(4')), 2.76(1H, brs, OH-4)。¹³C-NMR(100 MHz, CDCl₃) δ_c : 70.9(C-1), 68.1(C-2), 42.1(C-3), 69.9(C-4), 91.4(C-5), 75.6(C-6), 53.0(C-7), 76.2(C-8), 72.0(C-9), 54.1(C-10), 83.6(C-11), 29.6(C-12), 25.6(C-13), 24.6(C-14), 65.6(C-15); OAc-1: 169.5(C=O), 20.4(CH₃); OAc-2: 169.8(C=O), 21.1(CH₃); OAc-6: 169.5(C=O), 21.4(CH₃); OiBu: 175.8(C=O), 34.0(CH), 18.8(CH₃), 18.8(CH₃); O(α -Me)Bu: 176.6(C=O), 41.2(CH), 26.5(CH₂), 11.7(CH₃), 16.6(CH₃); OBz: 164.5(C=O), 128.3(C-1'), 130.2(C-2',6'), 128.5(C-3',5'), 133.8(C-4')。以上 NMR 数据与文献[10]报道的 1 β , 2 β , 6 α -triacetoxy-8 β -isobutanoyloxy-9 α -benzoyloxy-15-(α -methyl)butanoyloxy-4 α -hydroxy- β -dihydroagarofuran 数据一致,笔者称为苦皮素 P(angulatin P)。

化合物 9 白色无定形粉末。¹H-NMR(400 MHz, CDCl₃) δ_H : 5.47(1H, d, $J = 3.2$ Hz, H-1), 5.38(1H, m, H-2), 2.01(1H, dd, $J = 2.5, 15.0$ Hz, H-3a), 2.10(1H, m, H-3b), 5.22(1H, s, H-6), 2.56(1H, d, $J = 3.0$ Hz, H-7), 5.64(1H, dd, $J = 3.0, 9.8$ Hz, H-8), 6.06(1H, d, $J = 9.8$ Hz, H-9), 1.62(3H, s, H-12), 1.72(3H, s, H-13), 1.79(3H, s, H-14), 4.72(1H, d, $J = 13.2$ Hz, H-15a), 4.78(1H, d, $J = 13.2$ Hz, H-15b), 1.56 [3H, s, OAc-1(CH₃)], 2.09 [3H, s, OAc-2(CH₃)], 2.35 [3H, s, OAc-3(CH₃)], 2.37 [1H, sept, $J = 7.0$ Hz, OiBu-8(CH)], 0.90 [3H, d, $J = 7.0$ Hz, OiBu-8(CH₃)], 0.94 [3H, d, $J = 7.0$ Hz, OiBu-8(CH₃)], 7.85 [2H, m, OBz-9(2',6')], 7.42 [2H, m, OBz-9(3',5')], 7.55 [1H,

m, OBz-9(4')], 3.12(1H, br, OH-4), 5.22(1H, s, OH-6)。¹³C-NMR(100 MHz, CDCl₃) δ_c : 74.9(C-1), 67.3(C-2), 41.1(C-3), 72.1(C-4), 91.4(C-5), 76.9(C-6), 53.6(C-7), 73.4(C-8), 75.4(C-9), 50.6(C-10), 84.5(C-11), 30.0(C-12), 26.2(C-13), 24.2(C-14), 61.4(C-15); OAc-1: 169.6(C=O), 20.5(CH₃); OAc-2: 169.4(C=O), 21.1(CH₃); OAc-15: 170.3(C=O), 21.5(CH₃); OiBu: 175.9(C=O), 34.0(CH), 18.4(CH₃), 18.6(CH₃); OBz: 165.7(C=O), 129.2(C-1'), 129.4(C-2',6'), 128.6(C-3',5'), 133.4(C-4')。以上 NMR 数据与文献[11]报道的 1 β , 2 β , 15-triacetoxy-4 α , 6 α -dihydroxy-8 α -isobutanoyloxy-9 β -benzoyloxy- β -dihydroagarofuran 数据一致,笔者称为苦皮素 H(angulatin H)。

化合物 10 白色无定形粉末。¹H-NMR(400 MHz, CDCl₃) δ_H : 5.50(1H, d, $J = 3.9$ Hz, H-1), 5.34(1H, m, H-2), 1.96(1H, dd, $J = 2.6, 15.3$ Hz, H-3a), 2.20(1H, dd, $J = 4.7, 15.3$ Hz, H-3b), 6.81(1H, s, H-6), 2.44(1H, d, $J = 3.5$ Hz, H-7), 5.59(1H, dd, $J = 3.5, 6.5$ Hz, H-8), 5.63(1H, d, $J = 6.5$ Hz, H-9), 1.55(3H, s, H-12), 1.65(3H, s, H-13), 1.50(3H, s, H-14), 4.71(1H, d, $J = 13.6$ Hz, H-15a), 5.17(1H, d, $J = 13.6$ Hz, H-15b), 1.50 [3H, s, OAc-1(CH₃)], 2.05* [3H, s, OAc-2(CH₃)], 2.11* [3H, s, OAc-6(CH₃)], 2.13* [3H, s, OAc-8(CH₃)], 2.93 [1H, sept, $J = 7.0$ Hz, OiBu-15(CH)], 1.28 [3H, d, $J = 7.0$ Hz, OiBu-15(CH₃)], 1.29 [3H, d, $J = 7.0$ Hz, OiBu-15(CH₃)], 7.97 [2H, m, OBz-9(2',6')], 7.45 [2H, m, OBz-9(3',5')], 7.57 [1H, m, OBz-9(4')], 2.73(1H, brs, OH-4)。¹³C-NMR(100 MHz, CDCl₃) δ_c : 75.8(C-1), 67.8(C-2), 42.0(C-3), 69.7(C-4), 91.6(C-5), 75.4(C-6), 53.3(C-7), 69.8(C-8), 72.0(C-9), 53.0(C-10), 82.5(C-11), 29.3(C-12), 24.4(C-13), 24.3(C-14), 60.7(C-15); OAc-1: 169.6*(C=O), 20.3(CH₃); OAc-2: 169.6*(C=O), 20.9**(CH₃); OAc-6: 169.6*(C=O), 21.2**(CH₃); OAc-8: 170.1*(C=O), 21.5**(CH₃); OiBu: 177.3(C=O), 33.9(CH), 19.1(CH₃), 19.3(CH₃); OBz: 164.6(C=O), 129.1(C-1'), 129.5(C-2',6'), 128.7(C-3',5'), 133.6(C-4')。(*, ** 归属可互换)。以上

NMR 数据与文献 [12] 报道的苦皮藤素 III (celangulin III) 数据一致。

化合物 11 白色结晶。¹H-NMR (400 MHz, CDCl₃) δ_H: 5.46 (1H, d, J = 3.9 Hz, H-1), 5.34 (1H, m, H-2), 1.94 (1H, dd, J = 2.5, 15.1 Hz, H-3a), 2.19 (1H, dd, J = 5.0, 15.1 Hz, H-3b), 6.96 (1H, s, H-6), 2.39 (1H, d, J = 3.7 Hz, H-7), 5.57 (1H, dd, J = 3.7, 6.1 Hz, H-8), 5.64 (1H, d, J = 6.1 Hz, H-9), 1.56 (3H, s, H-12), 1.65 (3H, s, H-13), 1.48 (3H, s, H-14), 4.87 (1H, d, J = 13.6 Hz, H-15a), 5.07 (1H, d, J = 13.6 Hz, H-15b), 1.47 [3H, s, OAC-1 (CH₃)], 2.05* [3H, s, OAC-2 (CH₃)], 2.09* [3H, s, OAC-6 (CH₃)], 2.13* [3H, s, OAC-8 (CH₃)], 2.33 [3H, s, OAC-15 (CH₃)], 8.01 [2H, m, OBz-9 (2', 6')], 7.46 [2H, m, OBz-9 (3', 5')], 7.58 [1H, m, OBz-9 (4')], 2.70 (1H, br, OH-4)。¹³C-NMR (100 MHz, CDCl₃) δ_C: 76.0 (C-1), 67.8 (C-2), 41.9 (C-3), 69.7 (C-4), 91.7 (C-5), 75.0 (C-6), 53.2 (C-7), 69.8 (C-8), 72.0 (C-9), 52.9 (C-10), 82.6 (C-11), 29.3 (C-12), 24.3 (C-13), 24.1 (C-14), 60.2 (C-15); OAC-1: 169.5 (C = O), 20.3 (CH₃); OAC-2: 169.7 (C = O), 21.0* (CH₃); OAC-6: 169.5 (C = O), 21.2* (CH₃); OAC-8: 169.9 (C = O), 21.5* (CH₃); OAC-15: 170.5 (C = O), 21.6 (CH₃); OBz: 164.7 (C = O), 129.0 (C-1'), 129.5 (C-2', 6'), 128.7 (C-3', 5'), 133.6 (C-4')。 (* 归属可互换)。以上 NMR 数据与文献 [13-14] 报道的苦皮藤素 I (celangulin I) 数据完全一致, 笔者称为苦皮素 J (angulatin J)。

[参考文献]

[1] 中国科学院《中国植物志》编辑委员会. 中国植物志: 第 45 卷. 第 3 分册 [M]. 北京: 科学出版社, 1999: 102.
[2] 南玉生, 卢令娴. 植物杀虫剂苦皮藤研究现状 [J]. 农

药, 1995, 34(7): 28.

[3] 吴文君, 刘惠霞, 胡兆农, 等. 从天然产物到新农药创制——杀虫植物苦皮藤研究进展 [J]. 昆虫知识, 2008, 45(6): 845.
[4] Kou Y H, Chou C J, Kou Yang L M, et al. A sesquiterpene ester from *Celastrus hindsii* [J]. Phytochemistry, 1996, 41(2): 549.
[5] Wang M G, Chen F H. Sesquiterpene polyol esters from *Celastrus flagellaris* [J]. J Nat Prod, 1997, 60(6): 602.
[6] Huang H C, Shen C C, Chen C F, et al. A novel agarofuran sesquiterpene, Celahin D from *Celastrus hindsii* Benth [J]. Chem Pharm Bul, 2000, 48(7): 1079.
[7] Wu W J, Wang M G, Zhou W M, et al. Insecticidal sesquiterpene polyol esters from *Celastrus angulatus* [J]. Phytochemistry, 2001, 58(8): 1183.
[8] Wang M T, Qin H L, Kong M, et al. Insecticidal sesquiterpene polyol ester from *Celastrus angulatus* [J]. Phytochemistry, 1991, 30(12): 3931.
[9] Ji Z Q, Wu W J, Yang H, et al. Four novel insecticidal sesquiterpene esters from *Celastrus angulatus* [J]. Nat Prod Res, 2007, 21(4): 334.
[10] Wu W J, Wang M G, Zhu J B, et al. Five new insecticidal sesquiterpenoids from *Celastrus angulatus* [J]. J Nat Prod, 2001, 64(3): 364.
[11] Liu J K, Becker H, Zapp J, et al. Four sesquiterpenes from the insecticidal plant *Celastrus angulatus* [J]. Phytochemistry, 1995, 40(3): 841.
[12] Wu W J, Tu Y Q, Liu H X, et al. Celangulins II, III, and IV: new insecticidal sesquiterpenoids from *Celastrus angulatus* [J]. J Nat Prod, 1992, 55(9): 1294.
[13] 吴文君. 新化合物苦皮藤素 I 的分离及其生物活性 [J]. 西北农业大学学报, 1988, 16(2): 93.
[14] 吴文君, Wakabayashi N, Waters R M. 新化合物苦皮藤素 I 的结构鉴定 [J]. 西北农业大学学报, 1989, 17(4): 64.

[责任编辑 邹晓翠]